

Temperature Influence on the Stability and Chemical Composition of Electron Beam-Irradiated Polytetrafluoroethylene

K. SCHIERHOLZ,¹ U. LAPPAN,¹ A. PETR,² L. DUNSCHE,² K. LUNKWITZ^{1*}

¹Institute of Polymer Research Dresden, Dresden, Germany

²Institute of Solid State and Material Research Dresden, Dresden, Germany

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ABSTRACT: Polytetrafluoroethylene powder (PTFE) was exposed to electron beam radiation in presence of air. The irradiation mainly resulted in chain scission and induction of oxygenated groups and radicals as well as unsaturation. The thermal behavior of the irradiated PTFE and the fate of the radicals were studied comprehensively. Apart from fluorine, saturated and unsaturated fluorocarbons and oxygen-containing groups were released during heating. Furthermore, irradiation-generated peroxy radicals were transformed into alkyl radicals in a partly reversible process. A proposal for the complex reaction mechanisms of irradiated PTFE is given. The thermal stability of irradiated PTFE was improved by annealing. © 1999 John Wiley & Sons, Inc. *J Polym Sci B: Polym Phys* 37: 2404–2411, 1999

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INTRODUCTION

The unique structure of polytetrafluoroethylene (PTFE) causes properties that permit the use of the polymer in virtually every section of industry, for example, in apparatus engineering and electronic installations. On the other hand, the access to applications that require a higher polarity and energy of the surface, respectively, is prevented. In order to expand the scope of PTFE, modification of its properties by irradiation with accelerated electrons offers a comparatively cheap and easy-to-handle process that, in addition, is harmless to the environment. In presence of air, irradiation results in

formation of carbon fluoride, carboxyl groups, unsaturation, and peroxy radicals.^{1–6} Furthermore, the crystallinity of the material increases with rising irradiation dose. Contact angle measurements of PTFE-films after electron beam treatment have shown a change in surface energy.^{7,8}

However, electron beam-irradiated polytetrafluoroethylene is considerably less temperature-stable than unirradiated PTFE.⁹ The main reason for this effect is probably the high-energy radiation-induced chain degradation and the resulting release of short-chain fragments. Several researchers assume that radical reactions cause chain scission during heating of PTFE and contribute to further mass loss in this manner.^{1,2} Furthermore, it is questionable whether the thermal stability of the oxygenated groups (acid fluoride and carboxyl groups) is as large as it is in hydrocarbons because of the strong electron-withdrawing effect of the neighboring fluorine atoms, that speeds up decarboxylation.

In memoriam: Prof. Dr. sc. nat. Hans-Jörg Jacobsch
Present address: Institut für Polymerforschung Dresden e.V., Postfach 12 04 11, 01005 Dresden, Germany

*Correspondence to: K. Lunkwitz (E-mail: lunkwitz@argon.ipf.fld.dz)

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Generally, irradiated PTFE is used as additive in inks, plastics, finishes, and lubricants to provide nonstick and sliding properties as well as wear resistance.⁹ The suitability of irradiated PTFE as additive is not only due to the low molecular weight and the small particle size, but also to interactions between the oxygenated groups and other components of the polymer systems. It has been shown that high amounts of PTFE exposed to high-energy radiation can be incorporated into molten polyamides. One application of the obtained PTFE-PA block copolymers is for friction bearings. PTFE irradiated with high doses appeared to be especially suitable in this case. Information concerning the temperature behavior of irradiated PTFE is required to optimize the process of incorporation.¹⁰

The purpose of this work is to determine the structural origin of the thermal instability of irradiated PTFE and to provide a degradation mechanism. In order to achieve this aim, we monitored the thermal behavior of irradiated PTFE using simultaneous thermal analyses (STA) including mass spectroscopy, thermogravimetry (TG), IR spectroscopy, and electron spin resonance (ESR), respectively.

Usually, the number of functional groups and radicals formed during irradiation is small compared to the number of CF₂ groups. Changes in the chemical structure induced by postirradiation annealing can be detected the more accurate the higher the concentrations of the changed atoms or molecules are. Since the concentration of functional groups and radicals increases with irradiation dose, we investigated samples exposed to comparatively high doses.

EXPERIMENTAL

Polytetrafluoroethylene (Hostaflon TF1760, Hoechst AG) was used as received. Irradiations were performed in presence of air with a universal electron beam accelerator (1 MeV, ELT 1.5, Institute of Nuclear Physics, Novosibirsk). A transport system, which ensures a step-by-step irradiation with a dose of 0.2 MGy per pass, was used.

The exact increase in temperature was not measured during irradiation, since electronic temperature measurement devices do not work in the sphere of influence of high-energy radiation.

On the assumption that all of the energy was absorbed as thermal energy, the temperature difference is given by

$$\Delta T = D/C_p \quad (1)$$

where D is the absorbed dose and the heat capacity. Considering the dependence on temperature, C_p can be written as

$$C_p = 0.9324 + 0.001057T^{11} \quad (2)$$

The temperature after the first 0.2 MGy irradiation step can then be calculated by integration of

$$Q = \int_{T_0}^{T_f} C_p dT \quad (3)$$

where Q is the amount of heat (200 kJ/kg) and T_f the starting temperature (293 K).

Thus, we could estimate the heating-up of the PTFE specimens during the first irradiation step (0.2 MGy) to be approximately 140°C. Unfortunately, increase of temperature during further irradiation steps cannot be estimated exactly since T_f depends on the cooling rate of the irradiated PTFE powder that is again not known. We suppose that during irradiation with doses of more than 1 MGy, temperatures rose to at least 200°C.

Following irradiation, the PTFE powder was stored for about 2 years to avoid a falsification of analytical results that might have been due to reactions of activated species in the material prior to or during analyses. Beyond that, we compared the TG and ESR data of the stored PTFE powder and PTFE powder irradiated previously. However, the results showed no significant differences between the PTFE samples.

Annealing of the specimen was performed with a CARBOLITE 12/38/400 tubular furnace in air.

The infrared spectroscopy measurements were carried out on a FT-IR spectrometer (BIORAD FTS 155). The PTFE powder was moderately pressed onto KBr discs at room temperature.

The X-band ESR spectra were recorded with an ERS 800 [Zentrum für Wissenschaftlichen Gerätebau (ZWG)] and a VARIAN V4500 spectrometer, respectively. The modulation amplitude was 0.1 mT and the microwave power 1.0 mW. Temperature variation in the range 40–250°C was carried out in a cavity dewar. The desired temperature was controlled by a ZWG TEL2 unit.

The simultaneous thermoanalyses (STA) was performed on a Netzsch STA 428 in conjunction with a quadrupole mass spectrometer (QMS 408)

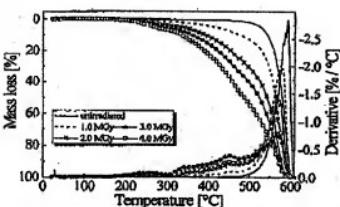


Figure 1. TG and DTG curves of irradiated PTFE (doses are given by the legend).

in a temperature range of 30–500°C and a heating rate of 5 K/min. Separation of the sampled degradation products by gas chromatography was not possible owing to apparatus conditions.

RESULTS AND DISCUSSION

TG

The mass loss vs. temperature curves for irradiated PTFE in nitrogen are shown in Figure 1. Whereas unirradiated PTFE, as it is well known, is stable up to 450°C and its degradation takes place in a single-stage process, irradiated PTFE is degraded in a multistage process. The derivatives of the mass loss vs. temperature curves, also shown in Figure 1, indicate a first degradation step between 200 and 300°C. We considered that only the first degradation step could be influenced, because the processes leading to further degradation are too complicated. So, the specimens were annealed at 150, 200, and 250°C, respectively, for 1–6 h in a tubular furnace prior to thermoanalyzes. Processes responsible for the increased mass loss in this temperature region should have been completed at the end of the annealing period.

The onset of degradation is shifted to at least the annealing temperature (Fig. 2). A temperature of 250°C and annealing time of 60 min was sufficient to eliminate the first degradation step in most cases. It is noticeable that annealing of powders irradiated with higher doses (2 and 4 MGy) at 150°C enhances the mass loss compared to unannealed powder. Above 300–350°C (i.e., beyond the first degradation maximum), the curve

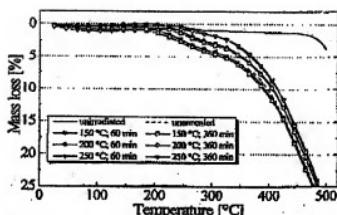


Figure 2. TG curves of irradiated and annealed PTFE (dose 2 MGy; unirradiated sample is given for reference).

for unannealed powder is more gradual in slope than the curves for powders that are annealed at 200 and 250°C, respectively. It is likely that the diffusion of short chain fragments through the bulk to the surface as well as the desorption from the surface are promoted by annealing. Further study is required to elucidate this point.

In a second test series, the mass loss was recorded isothermally at 250°C for 12 h (Fig. 3). In nitrogen, the mass loss is between 1.7 (1 MGy) and 11.2% (4 MGy). With less than 1 MGy, irradiated PTFE powders lose not even 1% of their mass. The mass loss rate of the powders between 6.5 and 12 h is constant (0.18%/h). No dependence on the irradiation dose was found here. The total mass loss shows an exponential growth for doses from 0 to 1 MGy. Above a dose of 1 MGy, it grows linearly (regression coefficient: 0.9993).

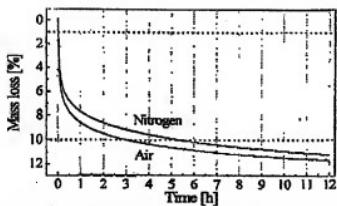


Figure 3. Mass loss of PTFE (4 MGy) irradiated in air and nitrogen.

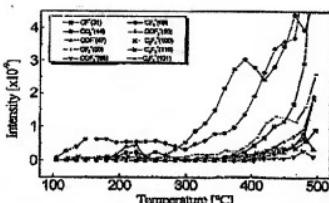


Figure 4. Thermal degradation products of PTFE irradiated with a dose of 2 MGy (30–500°C).

In some cases, the powder was annealed using a tubular furnace prior to TG. This means that the specimens were in contact to air during the heating process. In order to find out to what extent annealing was influenced by the presence of air, we recorded the isotherms of PTFE powder at 250°C in air. The shape of the deviations suggests that in the first 10 min, the degradation rate in presence of oxygen is higher than in nitrogen (Fig. 3). After approximately 1 h, the degradation of the powder annealed in nitrogen is higher. In both cases, 1% of the mass is lost after 1.5 min. The point of 10% mass loss is reached in air twice as fast as in nitrogen. The total mass loss is slightly higher in air than in nitrogen.

MS

The thermal degradation products of irradiated PTFE powder were measured in dependence on temperature by mass spectroscopy. As shown in Figure 4, oxygen-containing fragments could be found as well as C_xF_y fragments. The higher the irradiation dose, the lower is the temperature at which the first signals are detected (not shown in Fig. 4). In the dose range of 0.4–4 MGy, the initial temperature of appreciable $C_xF_y^+$ evolution is shifted from 400 to 300°C. In contrast to $C_xF_y^+$ and COF_2^+ ion curves (*m/e* 85), that show an almost exponential growth, the signals of CO_2^+ , CO^+ , and COF_2^+ (*m/e* 44, 47, and 68) have an additional peak between 190 and 230°C beside the main peak beginning between 300 and 400°C. The temperature range of the first peak corresponds to the range of the first degradation step mentioned previously. It is reasonable to assume that the COF^+ signal mainly originates from frag-

ments due to fluorine separation, since both signals are very similar in shape. The formation of CO_2^+ can be attributed to decarboxylation and a secondary reaction of COF_2 and water.



The strong abundance of the mass signal for *m/e* 69 is attributed to CF_3^+ ions due to fluorine migration during heating by Morelli et al.¹²

According to the literature, release of *m/e* 85 ions can be attributed to SIF_6^+ due to HF etching of glass material.⁶ As we did not use any glass material, we assume that *m/e* 85 ions most likely originate from the resection of $\cdot CF_2$ with $\cdot O-CF_2$ and subsequent cleavage of the O—CF₂-bond. Another possibility is the addition of $\cdot F$ to $\sim CF_2-OO-(O-CF_2)$ (Fig. 9) and subsequent cleavage of the O—O-bond. Both processes lead to formation of $\cdot O-CF_3$ giving rise to the discussed mass signal.

Annealing of the powder prior to analyses has a distinct influence on its degradation behavior. The signal intensity of nearly every degradation product is increased. A rise of the first peak of oxygen-containing fragments (190–230°C) after annealing at 150°C can be observed but, on the other hand, none of these fragments can be detected after annealing at 200 and 250°C, respectively [Fig. 5(a–c)].

IR

Exposure of PTFE to electron beam radiation leads, in presence of air, to the formation of oxygen-containing groups. Carboxyl and carbonyl fluoride groups could be identified by IR spectroscopy. The corresponding C=O stretching vibrations are located at 1810 ($\sim COOH^{new}$), 1776 ($\sim COOH^{old}$)¹³ and 1884 cm^{-1} ($\sim COF$),¹⁴ respectively. The band intensities rise with increasing irradiation dose. As shown in Figure 6, the acid bands are increased by annealing at 150°C. This effect, due to hydrolysis of the carbonyl fluoride groups by moist air, can be intensified by raising the temperature to 200 and 250°C, respectively. The influence of vacuum and various atmospheres on the oxygen-containing groups in the course of annealing is discussed elsewhere.

ESR

After irradiation of PTFE in presence of air, two different peroxy radicals (mid-chain and end-

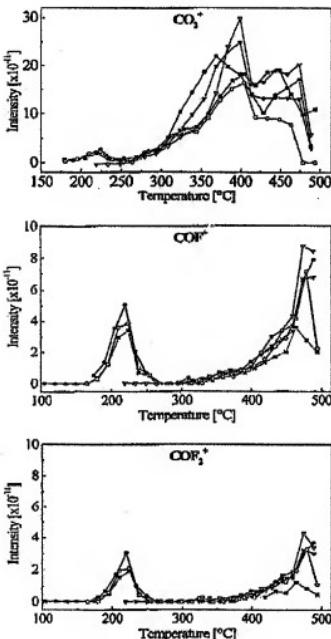


Figure 5. Temperature dependence of CO_2^+ (a, top), COF^+ (b, middle), and COF_2^+ (c, bottom) release. —■— unannealed, —●—150°C/60 min, —○—150°C/360 min, —▽—250°C/60 min, —▼—250°C/360 min.

chain) can be observed.¹⁵ The ESR spectra and total spin numbers of unannealed PTFE powder irradiated with different doses are shown in Figure 7. The spectra consist of two overlapping signals due to the two peroxy radical species. The spin numbers show a maximum at 1 MGy. That is due to partial decay of the radicals in consequence of the heating-up of the material during irradiation.

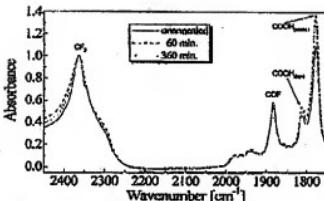


Figure 6. IR-spectra ($1750\text{--}2450\text{ cm}^{-1}$) of irradiated PTFE (dose 1 MGy) annealed at 150°C.

The thermal behavior of the mid-chain and end-chain peroxy radicals was investigated in two different ways: (a) annealing within a tubular furnace followed by ESR, and (b) annealing within the cavity of an ESR spectrometer.¹⁶ In general, the radicals are destroyed if the temperature is increased above a certain limit value, which is dose-dependent. Radicals in PTFE powder, which was irradiated with higher doses, are less temperature-stable than radicals in powder irradiated with lower doses. The ESR signals of PTFE irradiated with a dose of 4 MGy (e.g., disappear already after a few minutes treatment at 200°C) but, on the other hand, PTFE powder irradiated with a dose of 0.4 MGy actually contains peroxy radicals after annealing for 6 h at 250°C. The signal intensity ratio of the two radical species is different in dependence on the way of annealing. Annealing within a furnace with subsequent stor-

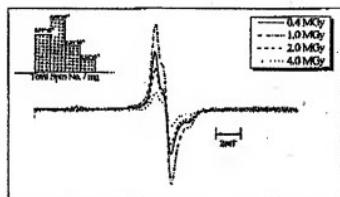


Figure 7. ESR spectra and total spin numbers of electron beam-irradiated PTFE powder in dependence on the dose.

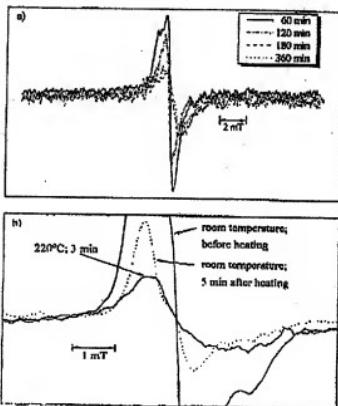
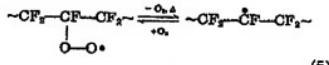


Figure 8. ESR spectra of PTFE annealed within a tubular furnace (a, top), and within the spectrometer cavity (b, bottom) for different times.

ing of the specimen produces an ESR signal that is dominated by the end-chain radical [Fig. 8(a)]. The shape of the signal obtained during annealing within the ESR cavity at elevated temperatures mainly corresponds to the shape of the pure mid-chain radical signal which was described by Iwasaki¹¹ [Fig. 8(b)]. Except from storing time, no differences in treating of the specimens were made. Before recording the ESR-spectra of the furnace annealed powder, the specimens were stored for 30 days. Within this time, the mid-chain peroxy radicals were converted into end-chain peroxy radicals (Fig. 9). The less temperature stable (i.e., more reactive) end-chain peroxy radicals disappear faster while annealing the PTFE powder. The raised reactivity of the end-chain radicals is due to their exposed position in the amorphous chain loops. Both radicals were found to be thermally stable up to 40°C in the case of an irradiation dose of 4 MGy only. The ESR signals of the peroxy radicals become weaker while raising the temperature. Finally, only the ESR signal attributed to mid-chain peroxy radicals can be detected. We assume

that the corresponding mid-chain peroxy radicals are located within the crystalline phase of the polymer, nearly unmovable, and, therefore, inaccessible for other radicals for recombination. Further raising of temperature leads to a transformation of the mid-chain peroxy radicals into the corresponding alkyl radicals, as the hyperfine splitting of the spectra shows (Fig. 10). It is worth mentioning, that this process is partly reversible.



The results presented so far indicate the complexity of the processes leading to the decrease in thermal stability of irradiated PTFE. Apart from desorption of short-chain fragments originating from polymer chain degradation during irradiation, radical reactions are responsible for this effect. Peroxy radicals of PTFE are remarkably stable at room temperature since migration of the rigid polymer chains through the material is impeded. The radicals are almost trapped in the polymer. Only the small oxygen (and water) molecules are able to diffuse toward reactive chain sites. However, chain migration is promoted by a rise in temperature, so that recombination and degradation reactions are facilitated. Consequently, the number of radicals decreases in dependence on the temperature and crystallinity of PTFE as indicated by the ESR measurements. A suggestion for the general reaction mechanisms involved is shown in Figure 9(a) and (b). End-chain peroxy radicals originating from irradiation and radical reactions of mid-chain radicals, respectively, eliminate COF_2 leaving behind an alkyl radical, that may again react with peroxy radicals or oxygen. The corresponding polymer chains are shortened by one CF_2 -group in each of these cycles [Fig. 9(a)] in this manner. Generated mid-chain radicals are converted into carbonyl and carboxylic end groups, respectively, and end-chain alkyl radicals are created [Fig. 9(b)]. In general, irradiation-generated mid-chain and end-chain peroxy radicals are able to combine with both peroxy radical species in an intermolecular reaction. Furthermore, it is likely that an intramolecular reaction takes place resulting in the formation of end-chain peroxy radicals, as well as COF_2 in the case of end-chain radicals and COF -end groups in the case of mid-chain radicals. Since most of the reaction branches lead to the

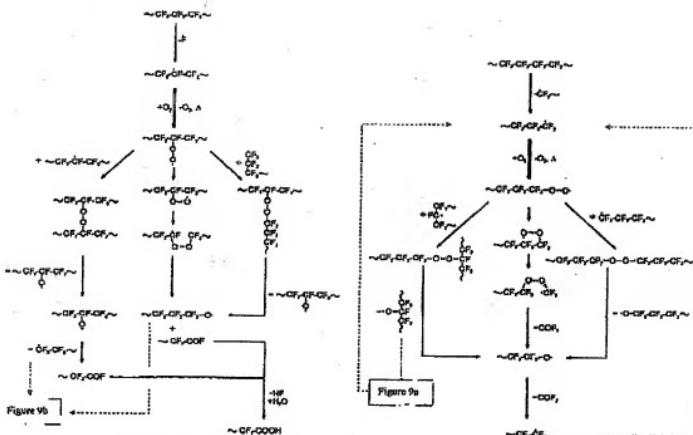


Figure 9. Radical-reaction scheme of irradiated PTFE. (a, left) Initial structure = mid-chain peroxy radical, and (b, right) initial structure = end-chain peroxy radical.

formation of end-chain alkyl radicals subsequently reacting with other peroxy radicals, the length of a radical-containing chain is reduced progressively.

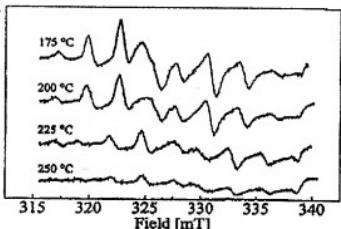


Figure 10. ESR spectra of alkyl radicals generated by heating of electron beam-irradiated PTFE (0.4 MGy).

CONCLUSIONS

The low-temperature stability of electron beam-irradiated PTFE can be attributed to two associated processes. On the one hand, radical reactions lead to partial decay of the polymer chains and, on the other hand, desorption of low-molecular weight compounds generated during irradiation is promoted by increasing the temperature.

Electron beam-irradiated PTFE powder shows a multistep degradation process. The first step due to decarboxylation and release of short chain fragments can be eliminated by annealing the powder at 250°C for 1 h. The degradation onset temperature is shifted to at least 280°C. The content of carboxyl and carbonyl fluoride groups was found to be increased by annealing.

Besides C₂F₅ fragments, oxygen-containing groups were found to be generated during heating. The main amount of the latter is CO₂ due to decarboxylation of the carboxyl groups and a secondary reaction of COF₂ with water.

Two different radical species can be observed after electron beam irradiation in air. Both mid-chain and end-chain peroxy radicals react very sensitively to increases in temperature. A certain portion of the mid-chain peroxy radicals is more temperature stable than the end-chain peroxy radicals are, due to their low mobility in crystalline structures.

The higher the irradiation dose, the less thermally stable the powders are and the faster the ESR signals disappear.

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